Received: 9 June 2011,

(wileyonlinelibrary.com) DOI: 10.1002/poc.1925

Kinetic and mechanistic study on the thermal isomerization of ocimene in the liquid phase

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Accepted: 18 July 2011,

The rate of thermal isomerization of ocimene in the liquid phase has been investigated in the range 90–150 °C. The rate constant for the disappearance of ocimene may be expressed by $k = 1.3 \times 10^{10} e^{-11994.2/T} (min^{-1})$, from which we can infer that the activation energy is 99.7 kJ mol⁻¹ and the pre-exponential factor is $1.3 \times 10^{10} min^{-1}$. The half-life for the disappearance of ocimene may be expressed by $t_{1/2} = 5.2 \times 10^{-11} e^{11994.2/T} (min)$. The conclusion has been supported by the study results that the ocimene is safe when temperature is below 100 °C. A discussion of the mechanism concerning the conversion is included. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: ocimene; allo-ocimene; kinetics; mechanism; isomerization

INTRODUCTION

Ocimene is an acyclic monoterpene found within a variety of plants and fruits. It has been found naturally as mixtures of the various forms. Ocimene exists as four isomers, and *allo*-ocimene also exists as four isomers. The mixture of ocimene is an oil with a pleasant odor. Thus, ocimene and its derivatives (ocimenol, esters and 6,7-expoxy ocimene, etc.) are mainly used as perfume components. In addition, they are widely used as building blocks for pharmaceuticals, flavors, fragrances, food supplements and pheromones.^[1-4] It is known that ocimene is obtained by thermal isomerization of α -pinene; however, under high temperature, ocimene has been intensively subjected to kinetic studies in gaseous, liquid or supercritical phase;^[7-9] however, the isomerization reaction of ocimene is rarely investigated.^[10-12]

The first work of this reaction was reported by Hawkins^[5] that the activation energy was 108.8 kJ mol⁻¹. Then, kinetic results were reported by Sasaki *et al.*^[10] that activation energy was 118.4 kJ mol⁻¹. Stolle *et al.*^[11] again investigated the pyrolysis of ocimene, and the activation energy was calculated to be 125.7 kJ mol⁻¹. Although many kinetic results have been published in the literature concerning the isomerization of ocimene, it seems to be appropriate to study the reaction once more from a kinetic and mechanistic point of view. Performing experiments with dipentene–ocimene mixtures under identical conditions allow for a detailed study. The calculation of activation parameters according to Arrhenius and Eyring equation are given.

EXPERIMENTAL

Materials

Standard samples are provided by the manufacturers. The mixtures of dipentene and ocimene are produced by fractional distillation the pyrolysis products from α -pinene. Other chemical reagents are purchased from Tianjin Guangfu Reagents Company.

Analyses

Analyses of the contents of products are carried out in a GC112A series. Products are identified by comparing the retention times and mass spectra with those compounds.^[13] GC112A-FID: SE-54 15 m × 0.25 mm 0.33 μ m capillary; program, 65 °C (hold 25–30 min); injector temperature, 250 °C; detector temperature, 250 °C. Results are treated with an N2000 workstation (Zhejiang University, Hangzhou, China) by the method of area normalization. TRACEDSQ (Thermo Finnigan, US) GC-MS: program, 65 °C (hold 2 min), 1 K/min up to 75 °C (hold 2 min), 30 K/min up to 150 °C (hold 2 min); injector temperature, 230 °C; carrier gas He, El(70 eV). Now we use the statistical software R version 2.11.1 (University of Auckland, New Zealand) to calculate linear regression equations by the method of the least squares.

Kinetic experiments

Kinetic experiments with the mixture of dipentene and ocimene were conducted. The mixture 20.00 g (25 ml) was added 0.2–0.5% inhibitor butylated hydroxytoluene (BHT), then protected by nitrogen. The mixture was heated at constant temperature in an oil bath, with a maximum variation of ± 1 °C at each temperature. At regular intervals, about 0.05 ml was quickly drawn from the sample with a syringe, then diluted with precooled acetone to 0.50 ml to quench the reaction. Finally, the rate of reaction was calculated according to the results from gas chromatography.

RESULTS AND DISCUSSION

Calculation of the rate of reaction

Kinetic experiments with the mixture of dipentene and ocimene were conducted at 141.5 $^\circ C.$ The plot is depicted in Fig. 1. The

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Scheme 1. Reaction products resulted from the thermal isomerization of $\alpha\mbox{-pinene}$

rate of the consumption of ocimene was fast at 141.5 °C, the half-life of the reaction was about 190 min according to Fig. 1.

Calculation of the rate constant

Hawkins^[5] first reported that the thermal isomerization of ocimene was a first-order reaction. From the first-order kinetic equation, the rate constant for the reaction is calculated by Eqn (1).

$$\ln w = -kt + \ln w_0 \tag{1}$$

where k is the rate constant for the consumption of ocimene, w is the weight fractions of ocimene at a certain time t, w_0 is the weight fractions of ocimene at the beginning of the reaction. Graphical methods can be employed to test Eqn (1) and to obtain the rate constant. The plot is depicted in Fig. 2.

Results suggest that the isomerization of ocimene is approximately a first-order reaction at 141.5 °C. The rate constant is calculated to be $3.619 \times 10^{-3} \text{ min}^{-1}$, and the value of the half-life is calculated to be 191.5 min, approaching the experimental resuzlts.

Effect of temperature on isomerization of ocimene

According to Eqn (1), kinetic experiments were investigated at different temperatures. The rate constant and the half-life were calculated, and then summarized in Table 1.

From Table 1, we can see that the rate constant is increased with increasing temperature. This relationship can be expressed by the Arrhenius equation

$$k = A e^{-E_a/RT} \tag{2}$$

To test the Arrhenius Eqn (2), we can take logarithms of both sides:

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$$n k = \ln A - E_a/RT$$
(3)



Figure 1. The content of each compound depending on the time at 141.5 $^\circ\text{C}$



Figure 2. The relationship lnw of ocimene and t

If the Arrhenius law applies, a plot of ln k against 1/T will be a straight line, and the slope will be $-E_a/R$. The plot is depicted in Fig. 3. Results suggest that the activation energy for the isomerization of ocimene is independent of the reaction temperature within the range of 90–150 °C. The activation energy for the isomerization of ocimene is calculated to be 99.7 kJ mol⁻¹; the pre-exponential factor is calculated to be 1.3×10^{10} min⁻¹.

The dependence of the rate constant of the reaction may be expressed by Eqn (4)

$$k = 1.3 \times 10^{10} \mathrm{e}^{-11994.2/T} (\mathrm{min}^{-1})$$
 (4)

The dependence of the half-life of the reaction may be expressed by Eqn (5)

$$t_{1/2} = 0.693/k = 5.2 \times 10^{-11} e^{11994.2/T} (min)$$
 (5)

Graphical methods can be employed to test the (5). When the half-life for the isomerization of ocimene is plotted against reaction temperature, we can obtain a simulative curve. The plot is depicted in Fig. 4.

Generally, the preparation of ocimene is conducted by the pyrolysis of α -pinene.^[5,6] According to Eqn (5), the half-life for the reaction is calculated to be only 0.7 s when the pyrolysis temperature is conducted generally about 350 °C. If a desirable product is ocimene, the pyrolysis products have to be cooled sharply. However, through general pyrolysis apparatus, for example a heated tube, pebble reactor or fluidized bed, the product of allo-ocimene rather than ocimene is obtained, because of the thermal isomerization of the ocimene initially produced.^[5,6,11,14,15] There has been no satisfactory solution to the problem of cooling the pyrolysate molecules sufficiently quickly to the temperature at which there is no appreciable reaction. The temperature at which there is no appreciable reaction is known as the safe temperature. We suggest that ocimene is safe when temperature is below 100 °C. Thus, we designed the pyrolysis apparatus to produce the thermally unstable ocimene. The pyrolysis apparatus is shown in Fig. 5.

In addition, the reaction mixture of α -pinene is then subjected to fractional distillation under vacuum in a Φ 25 mm \times 1500 mm column and then the qualified product can be obtained. We suggest that the boiling temperature of the reaction mixture of α -pinene is kept at below 100 °C under vacuum.

Table 1. The rate constants at different temperatures ^a										
T (°C)	$k ({\rm min}^{-1})$	t _{1/2} (min)	Simulative curve ^b	R ^{2 c}	<i>p</i> -value ^d					
90.5 102	6.025×10^{-5} 2.030×10^{-4} 1.210×10^{-3}	11,503.7 3414.3	$\ln w = -6.025 \times 10^{-5} t + 3.290$ $\ln w = -2.030 \times 10^{-4} t + 3.227$ $\ln w = -2.030 \times 10^{-4} t + 3.227$	0.9827 0.9742	$1.347 imes 10^{-5}$ $3.658 imes 10^{-5}$ $7.702 imes 10^{-8}$					
112 125.5 141.5	1.219×10^{-3} 1.219×10^{-3} 3.619×10^{-3}	2026.6 568.6 191.5	$\ln w = -3.420 \times 10^{-3} t + 3.213$ $\ln w = -1.219 \times 10^{-3} t + 3.174$ $\ln w = -3.619 \times 10^{-3} t + 3.067$	0.9647 0.9839 0.9947	7.702×10^{-12} 3.974×10^{-12} 7.383×10^{-14}					

^aThe content of ocimene in the mixture is 24–25%.

^{b,c,d}Calculated by the statistical software R version 2.11.1.



Figure 3. The plot of ln k against 1/T



Figure 4. The plot of the half-life depending on *T*

Mechanism of the isomerization of ocimene

The thermal isomerization of ocimene has been recognized for a long time; the mechanism for the rearrangement was proposed by Sasaki *et al.*^[10] Deuterium-labeling experiments performed by Gajewski *et al.*^[16,17] supported the hypothesis that the thermal isomerization of ocimene proceeded as 1,5-hydrogen shift reaction. Stolle *et al.*^[11] reported that activation entropy and frequency factor indicated a tight transition state, being typical for reactions passing through a six-membered ring transition state (Scheme 2). Because the proton in ocimene is bisallylic, the reaction probably is carried out through the carbon anion intermediate or the allylic radical intermediate (Scheme 2).

Kinetic experiments are investigated at different conditions to test those possible mechanisms. Results are summarized in

Table 2. Results indicate that the rate constant of the reaction is independent of the diluent of dipentene; a strong base catalyst (for example potassium *tert*-butyl alcohol); or an inhibitor (for example BHT). Thus, the isomerization of ocimene falls into the category of concerted pericyclic reaction in which there are no intermediates and proceeds through cyclic transition structures. In addition, the rate constant is also calculated by use of transition-state theory. The entropy of activation, enthalpy of activation and Gibbs energy of activation are calculated according to the Eyring equation (6).

$$k = (k_{\rm B}T/h)\exp(\bigtriangledown^{\ddagger}S/R)\exp(-\bigtriangledown^{\ddagger}H/RT)$$

= $(k_{\rm B}T/h)\exp(-\bigtriangledown^{\ddagger}G/RT)$ (6)

where $k_{\rm B}$ is the Boltzmann constant and h is the Planck constant. According to the Eyring equation (6), we can obtain the equations

$$\ln k = \ln(k_{\rm B}T/h) - \bigtriangledown^{\ddagger}G/RT \tag{7}$$

$$\ln A = \ln(k_{\rm B}T/h) - \nabla^{\ddagger}S/R \tag{8}$$

$$\nabla^{\ddagger} H = \nabla^{\ddagger} G + T \nabla^{\ddagger} S \tag{9}$$

$$E_{\rm a} = \bigtriangledown^{\ddagger} H + RT \tag{10}$$

At 125.5 °C, Gibbs energy of activation is calculated to be 107.9 kJ mol⁻¹; entropy of activation is calculated to be $-19.7 \text{ J} \text{ k}^{-1} \text{ mol}^{-1}$; enthalpy of activation is calculated to be 100 kJ mol⁻¹; activation energy is calculated to be 103.3 kJ mol⁻¹, while the experimental result is 99.7 kJ mol⁻¹. Activation entropy indicates a tight transition state, being typical for reactions passing through a six-membered ring transition state.^[11]

The conservation principle of the molecular orbital symmetry proposed by Woodward and Hoffmann and the frontier orbital theory proposed by Kenichi Fukui interpret perfectly the isomerization of ocimene. The six-membered ring transition state and molecular orbital are given in Scheme 3. According to the Woodward and Hoffmann rules, 1,3-hydrogen shift is forbidden, while 1,5-hydrogen shift is allowed. The thermal 1,5-hydrogen migration of ocimene is shown in Scheme 4.

CONCLUSION

The rate of thermal isomerization of ocimene in the liquid phase is investigated in the range 90–150 $^\circ\text{C}.$ The rate constants for the





Figure 5. (a) Apparatus for the preparation of ocimene by pyrolysis of α -pinene: (1) charging flask; (2) and (6) thermometer; (3) distillation column Φ 25 mm × 500 mm; (4) joint; (5), (8), (9) condenser; (7) thermocouple; (10) heating cage; (11) return line; (12) nichrome wire; (13) glass frame; and (14) magneton. (b) and (c) show a more detailed view of the condenser and heating cage (Φ 30 mm × 75 mm), respectively



Scheme 2. Three kinds of possible mechanisms of the thermal rearrangement of ocimene to allo-ocimene

Table 2. The rate constants of the reaction under different condition ^a											
Content of ocimene (%) Cat.(w%)		$k ({\rm min}^{-1})$	Simulative equation ^b	R ^{2 c}	<i>p</i> -value ^d						
24–25	0.2% BHT		1.219×10^{-3}	$\ln w = -1.219 \times 10^{-3} t + 3.174$	0.9839	$3.974 imes 10^{-12}$					
35–36	0.2% BHT		9.563×10^{-4}	$\ln w = -9.563 \times 10^{-4} t + 3.504$	0.9833	$\textbf{3.247}\times\textbf{10}^{-10}$					
35–36	0% BHT		$9.165 imes10^{-4}$	$\ln w = -9.165 \times 10^{-4} t + 3.471$	0.9874	8.272×10^{-12}					
35–36	0.5% (CH ₃) ₃ COK and (CH ₃) ₃ COH		$1.025 imes 10^{-3}$	$\ln w = -1.025 \times 10^{-3} t + 3.518$	0.9950	$5.06 imes 10^{-14}$					
^a Reaction temperature 125.5 °C. ^{b,c,d} Calculated by the statistical software R version 2.11.1. The average value of $k = 1.0 \times 10^{-3}$ (min ⁻¹).											
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Scheme 4. The thermal 1,5-hydrogen migration of ocimene

first-order reaction may be expressed by $k = 1.3 \times 10^{10} e^{-11994.2/T}$ (min⁻¹), and the activation energy is calculated to be 99.7 kJ mol⁻¹. We suggest that the ocimene is safe when temperature is below 100 °C. Thus, we design the apparatus for the preparation of ocimene by the pyrolysis of α -pinene. We suggest that the boiling temperature of the reaction mixture of α -pinene is kept at below 100 °C under vacuum. The experiment results indicate that the rate constant of the reaction is independent of the diluent of dipentene, a strong base catalyst (for example potassium *tert*-butyl alcohol) or an inhibitor (for example BHT). The mechanism of the isomerization of ocimene probably undergoes the 1,5-hydrogen shift pathway.

Acknowledgments

We thank Professor Xiangyang Tang for support of this work and Professor Tong Lin for his GC-MS expertise.

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